AN ROINN OIDEACHAIS

LEAVING CERTIFICATE EXAMINATION, 1997

09913

CHEMISTRY — HIGHER LEVEL

WEDNESDAY, 25 JUNE — AFTERNOON 2.00 to 5.00

Question 1 and **five** other questions must be answered. These five *must* include question 2 or question 3 but may include *both* question 2 and question 3.

All questions carry the same number of marks.

Relative atomic masses: H = 1, C = 12, N = 14, O = 16, Na = 23, Mg = 24, K = 39, Cr = 52, Fe = 56, I = 127.

Avogadro constant = 6×10^{23} mol^{-1}.

Molar volume at S.T.P. = 22.4 dm^3

1 Faraday = 96,500 C

1. Answer *eleven* of the following items (*a*), (*b*), (*c*), etc. All items carry the same number of marks. *Keep your answers short.*

    (*a*)   How many (i) electrons, (ii) neutrons, are there in the ion $_{31}^{70}\text{Ga}^{3+}$?

    (*b*)   What is (i) the conjugate acid of the sulphate ion, (ii) the conjugate base of nitric acid?

    (*c*)   How many atoms of hydrogen are there in 280 cm^3 of butane gas at S.T.P.?

    (*d*)   What are the *two* conditions that groups of three elements (e.g. Li, Na, K) must satisfy in order to be regarded as triads in Dobereiner's classification of the elements?

    (*e*)   Write an equation for the reaction that takes place when chlorine gas is bubbled through a solution containing bromide ions.

    (*f*)   Give the systematic (IUPAC) name of $CH_2BrCHBrCH_2CH_2OH$.

    (*g*)   A mass of 1.2 grams of magnesium ribbon dissolves more quickly in 50 cm^3 of a 1.5 mol dm^{-3} solution of sulphuric acid than in 150 cm^3 of a 0.5 mol dm^{-3} solution of sulphuric acid. Explain why this is so and indicate the number of moles of sulphuric acid used up in the reaction.

    (*h*)   State the shape of each of the following molecules: (i) CS_2, (ii) SCl_2.

    (*i*)   Distinguish clearly between homogeneous and heterogeneous catalysis.

    (*j*)   Name the nitrogen-containing product obtained (i) when sodium nitrate is heated, (ii) when calcium nitrate is heated.

    (*k*)   Express the concentration of a 10% (w/v) solution of potassium iodide in mol dm^{-3}.

    (*l*)   Give two factors which affect the rate of a chemical reaction.

    (*m*)   How would you show the presence of the thiosulphate ion in aqueous solution?

    (*n*)   Standard EDTA solutions are used in titrations to determine the hardness of water samples. What do the letters EDTA stand for? Name the indicator used in these titrations.

    (*o*)   Name a condensation polymer containing the linkage group shown.   — C — O —
            What is the general term for polymers containing this linkage group?   ‖
                                                                                                O
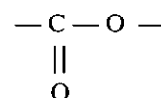
    (11 x 6)

2. The following experiment was carried out to estimate the percentage of ammonia, available as NH_4^+, in a fertiliser. A mass of 3.60 g of the crushed fertiliser was boiled with sodium hydroxide solution in a distillation flask fitted with a tap funnel. An excess of sodium hydroxide was used. The ammonia liberated was passed through a condenser and adaptor into a conical flask containing 100 cm^3 of a 1.0 mol dm^{-3} solution of hydrochloric acid. When all of the ammonia had been absorbed in the hydrochloric acid solution, the contents of the conical flask were transferred to a 500 cm^3 volumetric flask and made up accurately to the mark with deionised water. It was found by titration that 18.75 cm^3 of this solution exactly neutralised 25 cm^3 of a 0.06 mol dm^{-3} solution of sodium hydroxide. The equations for the reactions were

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O \quad ; \quad NH_3 + HCl \longrightarrow NH_4Cl \; ;$$
$$HCl + NaOH \longrightarrow NaCl + H_2O$$
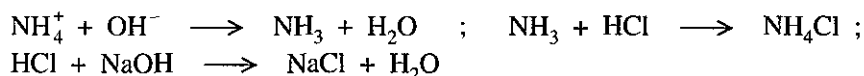
(i) Draw a labelled diagram of the apparatus used in liberating the ammonia from the fertiliser and absorbing it in the hydrochloric acid solution in the conical flask. (12)

(ii) Why was it necessary that the sodium hydroxide should be in excess in the reaction with the fertiliser? (6)

(iii) How would you have ensured that drops from the boiling mixture in the distillation flask did not get into the condenser? (6)

(iv) There is a tendency for the contents of the conical flask to be sucked back into the distillation apparatus. Explain why this is so and how you would deal with it if it began to occur. (9)

(v) List *three* precautions you would have taken in transferring the contents of the conical flask to the volumetric flask and making the solution up to the 500 cm^3 mark. (9)

(vi) Calculate the concentration of the hydrochloric acid solution in the volumetric flask in mol dm^{-3}. How many moles of hydrogen chloride were used up in the reaction with the ammonia liberated from the fertiliser? How many moles of ammonium ion (NH_4^+) were present in the fertiliser? (18)

(vii) Calculate the percentage by mass of ammonium ion (NH_4^+) in the fertiliser. (6)

3. A group of students prepared ethanoic acid by the reaction, in aqueous solution, between 9.2 cm^3 of ethanol (density 0.8 g cm^{-3}) and 35.76 g of sodium dichromate(VI), $Na_2Cr_2O_7.2H_2O$, acidified with excess sulphuric acid. The reaction mixture was boiled in a suitable apparatus for about thirty minutes, after which the ethanoic acid produced was recovered by distillation. After further purification the yield of ethanoic acid was found to be 47.4%. The equation for the reaction is

$$3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^+ \longrightarrow 4Cr^{3+} + 3CH_3COOH + 11H_2O$$
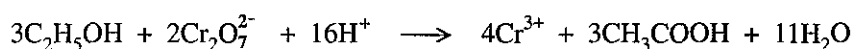
(i) Draw a labelled diagram of an apparatus that would have been suitable for boiling the reaction mixture. Explain (*a*) why the reaction mixture was boiled for some time before the distillation was carried out, (*b*) why this type of apparatus was used. (15)

(ii) State and explain what the students would have observed as the acidified dichromate solution reacted with the ethanol. (9)

(iii) The ethanoic acid obtained from the reaction mixture by distillation was impure. Name *two* impurities that were likely to have been present. (6)

(iv) Show clearly that there was an excess of sodium dichromate(VI) over ethanol in the experiment carried out by the students. Why was it important to have the oxidising agent in excess? (12)

(v) Calculate the volume of ethanoic acid (density 1.05 g cm^{-3}) obtained as a result of the experiment. (12)

(vi) Solutions of ethanoic acid can be titrated against solutions of strong bases. Name a suitable indicator for these titrations and state the colour change at the end-point. Explain why the indicator you have named changes colour at the end-point. (12)

4. Define (i) heat of combustion, (ii) kilogram calorific value, (iii) bond energy. (15)

A group of students carried out an experiment to measure the heat of combustion of propan-1-ol using the apparatus shown in the diagram. They burned 2 cm³ of propan-1-ol (density = 0.8 g cm⁻³), and assumed that all of the heat produced was absorbed by the 200 cm³ of water in the calorimeter. If the rise in temperature of the water was 47.6 K, calculate the value of the heat of combustion obtained by the students, given that the density and specific heat capacity of water are 1 g cm⁻³ and 4.2 kJ kg⁻¹ K⁻¹ respectively. (9)

An accurate value of the heat of combustion of propan-1-ol was got by burning 2 cm³ of the alcohol in a bomb calorimeter of heat capacity 7.5 kJ K⁻¹, the rise in temperature being 7.2 K. Calculate this accurate value for the heat of combustion of propan-1-ol. (9)
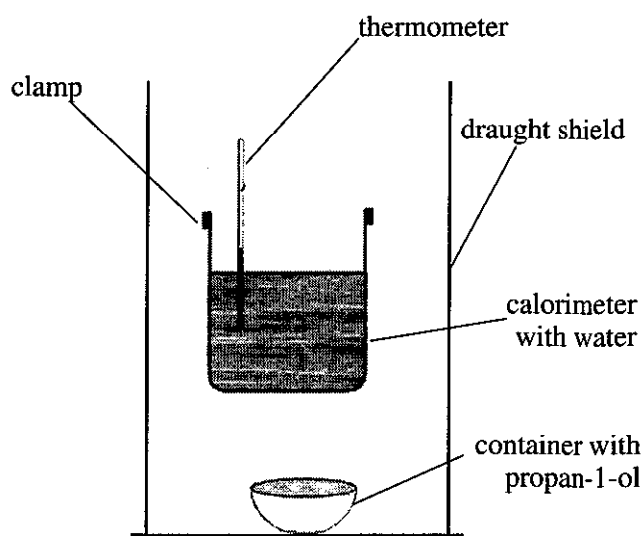
Suggest a reason for the inaccuracy in the student experiment, and use the accurate value of the heat of combustion to calculate the kilogram calorific value of propan-1-ol. (9)

Propene can be prepared from propan-1-ol in the laboratory. The equation for the reaction is

$$CH_3CH_2CH_2OH \longrightarrow CH_3CH=CH_2 + H_2O$$

Calculate the heat change (ΔH) for this reaction using the accurate value of the heat of combustion of propan-1-ol, and given that the heat of combustion of propene is -2058 kJ mol⁻¹. Outline briefly how the preparation of propene from propan-1-ol can be carried out in the laboratory. (18)

The heats of combustion of propan-1-ol and propan-2-ol are almost identical. Suggest, in terms of bond energy values, why this is so. (6)

5. Answer this question by referring where necessary to the first thirty-six elements of the Periodic Table (Mathematics Tables, p. 44 to p. 46).

(i) Define (a) atomic number, (b) mass number, (c) relative atomic mass, (d) electronegativity. (18)

(ii) Given that naturally-occurring silicon consists of 92.23% of $^{28}_{14}Si$, 4.67% of $^{29}_{14}Si$ and 3.10% of $^{30}_{14}Si$, calculate the relative atomic mass of silicon, giving your answer correct to two places of decimals. What is the reason for the difference in the mass numbers of the three isotopes? (9)

(iii) Use electronegativity values to predict the bonding (a) in phosphine (PH_3), (b) in phosphorus(III) chloride, (c) in potassium chloride. Write an equation for the reaction of the chloride in (b) with water. (15)

(iv) Show, by means of suitable diagrams, the formation of the bonds in potassium chloride and phosphine. Explain why potassium chloride has a much higher boiling point than phosphine. (15)

Phosphine is virtually insoluble in water whereas the corresponding hydride of nitrogen, which is in the same group as phosphorus, is very soluble in water. Why is this so? (9)

6. (i) Iron is both a <u>d-block element</u> and a <u>transition element</u>. Explain the underlined terms. Give *two* characteristic properties of transition elements. (12)

(ii) An oxide of iron contains 70% by mass of the metal. Work out the empirical formula for this oxide. What is the valence of iron in this oxide? Give the formula of another common oxide of iron in which the iron has a lower valence. (15)

(iii) Write the electronic configurations (s, p, etc.) for the iron ions in the two oxides in (ii) above. Which of the two ions would you expect to be the more stable? Give a reason for your answer. (12)

(iv) Oxides of iron are reduced in the manufacture of iron in the blast furnace. What is the main reducing agent? Show by means of equations how this reducing agent is produced in the blast furnace and how it reduces the oxide containing 70% by mass of iron. (15)

(v) What substance is added as part of the charge of the blast furnace in order to remove impurities such as silica (SiO_2) and alumina (Al_2O_3) which are commonly found in iron ores? In the case of *one* of these impurities show, by means of equations, the reactions that lead to its removal. What name is usually given to the material obtained as the end product of the removal process? (12)

7. (*a*) Describe briefly what takes place (i) in the primary treatment of sewage, (ii) in the secondary treatment of sewage. (12)

(*b*) What do you understand by the biochemical oxygen demand (B.O.D.) of a water sample? (6)

In determining the dissolved oxygen concentration of a water sample, the addition of two very concentrated solutions to the water sample resulted in the formation of a brown precipitate (Mn_2O_3). On acidification with sulphuric acid, this precipitate dissolved and an iodine solution was formed.

(i) Identify the two solutions that were added to the water sample. Explain why the solutions used were very concentrated. (9)

(ii) What experimental technique was used in adding the solutions to the water sample? Explain why this technique was used. (6)

(iii) What standard solution was used to determine the concentration of the iodine solution? Name the indicator that was used. (6)

(*c*) Define oxidation in terms of electron transfer and also in terms of change in oxidation number. (6)

In the dissolved oxygen concentration determination described in (*b*), the acidification with sulphuric acid resulted in the reaction represented by the following unbalanced equation.

$$H^+ + Mn_2O_3 + I^- \longrightarrow Mn^{2+} + I_2 + H_2O$$
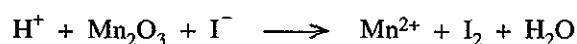
(i) Show that the reaction is an oxidation-reduction reaction. (6)

(ii) Identify the species oxidised and the species reduced in the reaction. (6)

(iii) Balance the equation. (9)

8. *(a)* Distinguish between substitution and addition reactions in organic chemistry. (6)

Addition reactions are the characteristic reactions of unsaturated compounds. What is meant by an unsaturated compound? (3)

Show, by means of an equation, a substitution reaction of a named alkane, and name the organic product of the reaction. Show, also by means of an equation, an addition reaction of a named alkene, and name the product of the reaction. (12)

Outline the mechanism of the reaction in the case of the substitution reaction of the named alkane. (12)

(b) The formulae of three organic compounds are

A	**B**	**C**

$$CH_3CHCHO$$
$$|$$
$$CH_3$$

$$CH_3CH_2COCH_3$$
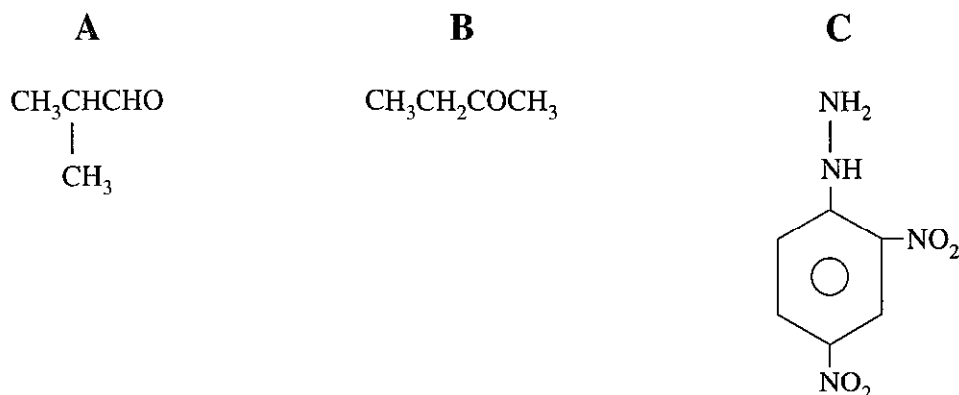
(i) Name each of the compounds **A**, **B** and **C**. (9)

(ii) **A** and **B** are structural isomers. Explain clearly what this means. (6)

(iii) Outline a chemical test to distinguish between compounds **A** and **B**. (9)

(iv) Give the name *and* structural formula of the organic product of the reaction between compound **B** and compound **C**. (9)

9. Explain the terms *reversible reaction* and *chemical equilibrium.* (12)

In the manufacture of sulphuric acid by the Contact Process, sulphur trioxide is produced from sulphur dioxide and oxygen in the presence of a mixture of vanadium(V) oxide and potassium sulphate, supported on pellets of silica. The vanadium(V) oxide acts as catalyst and the minimum working temperature is about 400 °C. When 50 moles of sulphur dioxide and 25 moles of oxygen were allowed to come to equilibrium at 400 °C and at a pressure of one atmosphere, the equilibrium mixture contained 49 moles of sulphur trioxide. The equation for the reaction is

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$$
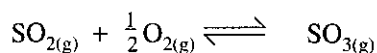
(i) What term is used to describe the function of the potassium sulphate in the mixture with vanadium(V) oxide? (6)

(ii) Write the equilibrium constant expression (K_p) for the reaction. (6)

(iii) Calculate the partial pressures of sulphur dioxide, oxygen and sulphur trioxide in the equilibrium mixture, giving your answers correct to two decimal places. Calculate also the value of K_p at 400 °C. What would the value of K_p have been if the following form of the equation had been used?

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

(24)

(iv) In some modern sulphuric acid plants, pressures of 4-7 atmospheres are used. State and explain the effects these higher pressures would have on the yield of sulphur trioxide at equilibrium. (9)

(v) Describe briefly how the sulphur trioxide is converted to sulphuric acid. (9)

10. Answer any *two* of the following.

(*a*) Define pH. (6)

Calculate the pH of

    (i) a nitric acid solution of concentration 0.1 mol dm^{-3}, (6)

    (ii) a solution containing 0.16 g of sodium hydroxide in 400 cm^3 of solution, (9)

    (iii) a solution obtained by adding 100 cm^3 of the nitric acid solution in (i) to 400 cm^3 of the sodium hydroxide solution in (ii). (12)

(*b*) The diagram shows the <u>electrolysis</u> of aqueous copper(II) sulphate using inert (platinum) electrodes.

    (i) Explain what is meant by the underlined term. (6)

    (ii) Identify the gas X and show, by means of an equation, how it is produced. (9)

    (iii) What change would you observe in the appearance of the electrolyte as the reaction proceeds? What is the reason for this change? (9)

    (iv) When a constant current of 10 amperes was passed through the electrolyte for t seconds, the volume of X produced was 28 cm^3 (measured at S.T.P.). Find the value of t. (9)
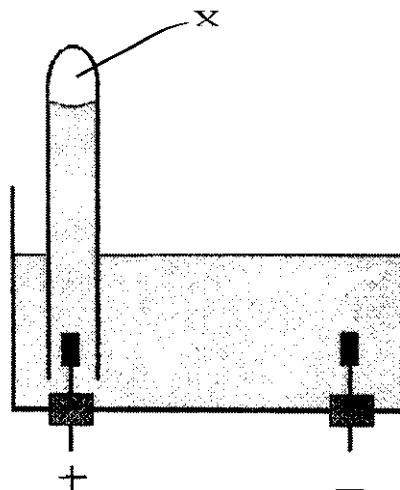
(*c*) In a simple catalytic cracking experiment using liquid paraffin, the paraffin was vaporised and the vapour was passed over a heated catalyst. This resulted in the production of colourless, flammable gases which were collected in test tubes over water.

    (i) What is catalytic cracking? Name a catalyst that could have been used in the experiment described above. (9)

    (ii) State any *two* benefits of catalytic cracking in the oil refining process. (6)

    (iii) Liquid paraffin is a mixture of different compounds. The molecular formula of one of these compounds is $C_{11}H_{24}$. Suppose that, as a result of the cracking experiment, a molecule of this compound gave an alkane molecule with two branches, a branched alkene molecule, and an unbranched alkene molecule. Write down the systematic (IUPAC) name and the structural formula of each of the three molecules obtained from the $C_{11}H_{24}$ molecule. (18)

(*d*) Define *ideal gas*. (6)

Give *two* reasons why real gases depart from ideal behaviour. (6)

Under what conditions of temperature and pressure do real gases come closest to ideal behaviour? In the case of *one* of these conditions, suggest a reason why it brings the gases closer to ideal behaviour. (12)

Use the molar volume of a gas at S.T.P. to show that the value of the gas constant (R), correct to two decimal placcs, is 8.31 J K^{-1} mol^{-1}. Standard pressure is 1.013×10^5 N m^{-2} and standard temperature is 273 K. (9)